Serial No. 10/526,474

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Koji TATSUMI et al.

Serial No. 10/526,474 : Group Art Unit: 1745

Filed: March 3, 2005 : Examiner: Ben LEWIS

For: POSITIVE ELECTRODE MATERIAL FOR LITHIUM SECONDARY BATTERY AND PROCESS FOR PRODUCING THE SAME

DECLARATION UNDER RULE 132

Hon. Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450

Sir:

I, Koji Tatsumi, having a post office address at c/o AGC SEIMI CHEMICAL CO., LTD. of 3-2-10, Chigasaki, Chigasaki-City, Kanagawa, 253-8585, Japan, hereby declare that I am a co-inventor of the above application; and

that I have conducted the following experiments under my supervision.

Experiment

Abstract

Regarding the positive electrode materials described in US Patent Application Serial No. 10/526,474 (present invention) and US Patent No. 6,071,645 (Biensan), a diffraction peak and a battery property at 2θ $28\pm1°$ were measured by a high-sensitivity X-ray diffractometry. As a result thereof, the positive electrode material described in the present invention did not have any diffraction peak at 2θ $28\pm1°$; and had a high discharge capacity and an excellent battery property. On the other hand, the

positive electrode material described in US Patent No. 6,071,645 had a diffraction peak at 2θ $28\pm1°$; a low discharge capacity; and a poor battery property.

Regarding the respective positive electrode materials which were obtained by synthesizing the positive electrode materials described in the present invention and US patent No. 6,071,645 (Biensan), the diffraction peak and the battery property at 2θ $28\pm1°$ were measured by a high-sensitivity X-ray diffractometry. The presence or absence of the diffraction peak and the battery property such as a discharge capacity of each positive electrode material were compared. As a result thereof, the positive electrode material described in the present invention did not have any diffraction peak at 2θ $28\pm1°$ and had a high discharge capacity. On the other hand, the positive electrode material described in US patent No. 6,071,645 had a diffraction peak at 2θ $28\pm1°$ and a low discharge capacity compared to the positive electrode material described in the present invention.

Experimental procedure

The experiments were conducted from Jan. 2008 to Feb. 2008 in AGC Seimi chemical Co. Ltd.

In the experiments, the positive electrode material was produced by the method described in the present invention in principle. Further details of the procedure are explained as follows.

Production and measurement of lithium composite cathode materials

Experiment 1

Predetermined quantities of cobalt oxyhydroxide powder having an average particle diameter D50 of 10.2 μm, wherein 50 or more primary particles were coagulated to form a secondary particle, lithium carbonate powder, magnesium hydroxide powder, and zirconium oxide powder were mixed. These four kinds of powders were dry-mixed, and then, fired at 850°C for 14 hours in the atmosphere. As a result of wet-dissolving the powder after firing, and measuring the content of cobalt, aluminum,

zirconium and lithium by ICP and atomic absorption spectrometry, the composition of the powder was $LiCo_{0.98}Mg_{0.01}Zr_{0.01}O_2$.

The $LiCo_{0.98}Mg_{0.01}Zr_{0.01}O_2$ powder thus obtained, acetylene black, and polytetrafluoroethylene powder were mixed in a weight ratio of 80/16/4, kneaded while adding toluene, and dried to fabricate a positive electrode plate of a thickness of 150 μm.

Then, by using an aluminum foil of a thickness of 20 μm as a positive electrode collector, using porous polypropylene of a thickness of 25 μm as a separator, using a metallic lithium foil of a thickness of 500 μm as a negative electrode, using a nickel foil of 20 μm as a negative electrode collector, and using 1M LiPF6/EC+DEC (1:1) as an electrolyte, a simple sealed cell made of stainless steel was assembled in an argon glove box.

The cell was first charged to 4.5 V using a load current of 75 mA for 1 g of the positive electrode active material at 25°C, and discharged to 2.75 V using a load current of 75 mA for 1 g of the positive electrode active material to obtain the initial discharge capacity and the initial efficiency.

In the initial discharge capacity at 25°C, 2.75 to 4.5 V, a discharge rate of 0.5 C was 183.5 mAh/g, and the initial efficiency was 92.0%.

The X-ray diffraction spectrum of the fired powder was obtained by a high-sensitivity X-ray diffractometry using Cu-K α ray, using a Model RINT2500 X-ray diffractometer manufactured by Rigaku Corporation under the conditions of an accelerating voltage of 50 kV, an accelerating current of 250 mA, a scanning speed of 1°/min, a step angle of 0.02°, a divergence slit of 1°, a scattering slit of 1°, a receiving slit of 0.3 mm, and monochromatization. The obtained spectrum is shown in FIG. 1. From FIG. 1, no diffraction spectrum at 2θ of $28 \pm 1°$ was observed, and it was found that zirconium was not present as a single-component oxide.

It was also found from the analysis of the X-ray diffraction spectrum that about 90% of the zirconium formed a solid solution with cobalt, and about 10% thereof was present as Li_2ZrO_3.

Experiment 2

A positive electrode active material was synthesized in the same manner as in Experiment 1 except that firing temperature was changed from 850°C to 750°C, and composition analyses, property measurements, and cell performance tests were carried out. As a result thereof, the composition was $LiCo_{0.98}Mg_{0.01}Zr_{0.01}O_2$.

In the initial discharge capacity at 25°C, 2.75 to 4.5 V, a discharge rate of 0.5 C was 180.3 mAh/g, and the initial efficiency was 90.5%.

The X-ray diffraction spectrum of the fired powder was obtained by a high-sensitivity X-ray diffractometry under the same conditions described in Experiment 1. And it was found that a quantity of zirconium was present as a single-component oxide.

Experiment 3

A positive electrode active material was synthesized in the same manner as in Experiment 1 except that mixing ratio of raw materials such as cobalt oxyhydroxide powder, lithium carbonate powder, magnesium hydroxide powder, and zirconium oxide power, and composition analyses, property measurements, and cell performance tests were carried out. As a result thereof, the composition was $LiCo_{0.90}Mg_{0.05}Zr_{0.05}O_2$.

The initial discharge capacity at 25°C, 2.75 to 4.5 V, and a discharge rate of 0.5 C was 165.7 mAh/g, and the initial efficiency was 91.3%.

The X-ray diffraction spectrum of the fired powder was obtained by a high-sensitivity X-ray diffractometry under the same conditions described in Experiment 1. And it was found that zirconium was evidently present as a single-component oxide.

Experiment 4

A positive electrode active material was synthesized in the same manner as in Experiment 3 except that fired temperature was changed from 850°C to 750°C, and composition analyses, property measurements, and cell performance tests were carried out. As a result thereof, the composition was $LiCo_{0.90}Mg_{0.05}Zr_{0.05}O_2$.

The initial discharge capacity at 25°C, 2.75 to 4.5 V, and a discharge rate of 0.5 C was 165.7 mAh/g, and the initial efficiency was 90.5%.

The X-ray diffraction spectrum of the fired powder was obtained by a high-sensitivity X-ray diffractometry under the same conditions described in Experiment 1. The obtained spectrum is shown in FIG. 1. From FIG. 1, diffraction spectrum at 2θ of $28 \pm 1°$ was significantly observed, and it was found that zirconium was evidently present as a single-component oxide.

Discussion of the obtained result

When high-sensitivity X-ray diffraction spectrums of the positive electrode materials obtained in Experiment 1 is compared to that of Exeriment 4 as described in Fig. 1, it is apparent that at 2θ $28 \pm 1°$, the positive electrode material obtained in Experiment 4 has a diffraction peak while the positive electrode material obtained in Experiment 1 does not have any diffraction peaks. In addition, data of a heat treatment temperature, early discharge capacity, and early efficiency regarding the positive electrode materials obtained from Experiments 1 to 4 are shown in the table, as follows.

	$LiCo_{0.98}Mg_{0.01}Zr_{0.01}O_2$			$LiCo_{0.90}Mg_{0.05}Zr_{0.05}O_2$		
Firing temperature	2θ $28 \pm 1°$ Diffraction peak	Early discharge capacity	Early efficiency	2θ $28 \pm 1°$ Diffraction peak	Early discharge capacity	Early efficiency
(°C)	-	mAh/g	%	-	mAh/g	%
750	Slightly present	180.3	90.5	Present	165.7	90.5
850	Not present	183.5	92.0	Present	165.7	91.3

As shown in the table, the positive electrode material obtained in Experiment 4 has both a low early discharge capacity and a low early efficiency, and it is apparent that the positive electrode material obtained in Experiment 4 is inferior to the positive electrode material obtained in Experiment 1.

More specifically, the positive electrode material, which was fired at 750 °C, has a high amount of zirconium and magnesium, and has a diffraction peak at 2θ $28\pm1°$, and the positive electrode material, which was fired at 850 °C, has an appropriate amount of zirconium and magnesium, and does not have any diffraction peak at 2θ $28\pm1°$. When the above-mentioned positive electrode materials are compared, there is an apparent difference as to a battery property.

In addition, even when the positive electrode material (Experiment 2), which was synthesized in the same manner as in Experiment 1 except that firing temperature was different; or the positive electrode material (Experiment 3), which was synthesized in the same manner as in Experiment 1 except that mixing ratio of raw materials was different, and the positive electrode material of the present invention are compared, there is a difference as to the presence of the diffraction peak at 2θ $28\pm1°$ in the high-sensitivity X-ray diffractometry as well as the significant differences as to the battery property.

Conclusion

The positive electrode material described in the present invention is different from that of US patent No. 6,071,645 (Biensan) as to the presence of a diffraction peak at 2θ $28\pm1°$ in a high-sensitivity X-ray diffractometry and a heat treatment temperature. In addition, due to the above-mentioned differences, it has been proven that the positive electrode material in the present invention has a battery property substantially better than that of US patent No. 6,071,645 (Biensan).

I have an opinion that the results afforded by the present invention are important and commercially significant, and that these results would not have been expected by one skilled in the art at the time the present invention was made.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine, or imprisonment, or both, under Section 1001 of

Serial No. 10/526,474

Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Koji Tatsumi

Koji Tatsumi

Mar. 21, 2008

Date